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A theoretical investigation of the role of polarization in the formation of hydrogen bonds

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With 14 figures in the text

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SUMMARY

The purpose of this investigation was to investigate the question of whether polarization energies ought to be taken into account when calculating hydrogen bond energies. Therefore the aim has been to get only the correct orders of magnitude, and not quantitative information, concerning these energies. The corresponding electrostatic energies have, for comparison, been estimated by means of rough models. In two of the cases investigated here, viz. H_2O and HF, the molecules of which form strong H bonds, the polarization energies were found to be of the same orders of magnitude as the total H bond energy. For H_2S and HCl, the molecules of which form no, or very weak, H bonds, the polarization energies were found to be negligible compared with the energy of a normal H bond. A preliminary report of this investigation has been published in *Acta Chem. Scand.* [22].

A. Introduction

It has been customary, for a long time, to consider the electrostatic interaction as the main factor contributing to the energy of hydrogen bonds (H bonds) [1]. As a rule, those molecules which contain polar groups form the strongest H bonds and this fact agrees fairly well with the theory of electrostatic binding forces. However, various experiments have shown that the electrostatic viewpoint is not sufficient for explaining the strengths of H bonds. In particular, two other factors should be taken into account, viz. covalent binding and polarization. Thus, the main factors which are operative in the formation of an H bond can be supposed to be: (1) electrostatic interaction, (2) covalent binding and (3) polarization.

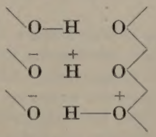
It is of course impossible to split up strictly the energy of a system into parts derivable from the electrostatic interaction, covalent binding, etc. Instead, these "parts" depend on each other in such a way that any one of them would not be the same if the others were absent. But, if the system in question is a stable one which has been perturbed in some way, then it is reasonable to neglect the mutual interactions of the different factors. The neglected effect may therefore be supposed to be of the second order in the perturbation parameter. To avoid the enormous computations which are required for complete quantum-mechanical calculations even on fairly simple systems, one tries to separate the effects in this way. An approximation of this type is more accurate the smaller the studied effects are.

The problems concerning chemical bonds are often such that an approximate method of the above-mentioned type gives at least qualitatively satisfactory results. Molecules are regarded as coaggregates of "free" atoms which perturb each other when the molecules are formed. Similarly, crystals and other compounds of two or more molecules can be regarded as "free" molecules interacting in some way.

Compounds containing H bonds are molecular systems of this kind. The energy bound in the H bonds is much smaller than both the total energy of the molecule and the energy bound in the "normal" chemical bonds. We are therefore justified in using models for these systems which consist of molecules with almost the same configuration as free ones and also in talking about "electrostatic" energy, "covalent binding" energy and "polarization" energy.

By means of a classical model and postulating the presence of electrostatic forces and polarization, Bauer and Magat [2] were able to compute with good results the spectra of compounds containing H bonds.

The role of covalent binding forces in H bonds has been investigated by Coulson and Danielsson [3, 4]. They considered a system O–H ··· O and assumed that it can be described as a superposition of the three configurations



(1)

Using this model, they found that, except for short bonds, the weight of the covalent structure was only 2–4 %. For short bonds, the covalent contribution became much more significant. Similar calculations have been performed by Tsubomura [5] who found a delocalisation energy for hydrogen-bonded water molecules which amounted to about 8 kcal/mole. This energy is due to the electron transfer from a proton-acceptor to a proton-donor which is represented by the two structural formulae $\overset{-}{O}\,H\text{–}\overset{+}{O}$ and $O\,\overset{-}{H}\text{–}\overset{+}{O}$. This 8 kcal/mole energy is therefore appreciably greater than the calculated electrostatic energy which has usually been considered to be the most important source of the binding force. These results show that it is not only the electrostatic energy which is of the same order of magnitude as the H bond energy.

In 1948, Ehrenberg and Fischer [6, 7] found experimentally that certain organic compounds with a less easily polarized heteroatom were less soluble in water than others with a more easily polarized heteroatom. Fischer [8] performed a rough quantum-mechanical calculation which indicated that, because of hydrogen bond formation, the molecules involved become polarized to a certain extent. It is likely that a gain in energy due to this polarization may play a part in the formation of the hydrogen bond. More thorough quantum-mechanical calculations, which could clarify the role of polarization in H bond formation, were proposed.

The aim of this work has been to investigate the polarization energy of H bonds. In order to make the computational work tolerable, it was necessary to make certain simplifications but the results should be of the right order of magnitude. It was not expected that more exact conclusions concerning the energies could be deduced.

The author has studied the associations of H_2O and HF, in which there are very strong H bonds, and for comparison the associations of H_2S and HCl in which there are no H bonds or at most very weak ones. The association energies which have been obtained experimentally are listed in Table 1 together with melting and boiling points. As is well-known, water and hydrogen fluoride exhibit, as far as melting and boiling points and heats of association are concerned, an abnormal behaviour in comparison with related substances [9].

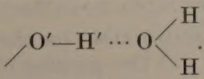
Table 1. Experimental melting points, boiling points and H bond energies for the substances studied here.

	Melting point °C	Boiling point °C	H bond energy kcal/mole
H_2O	0	100	5.8
H_2S	−83	−62	—
HF	−92	19	6.7
HCl	−112	−84	—

The present author wished to obtain results of comparatively high accuracy, especially for water and hydrogen fluoride. This desire could be realized because very good quantum mechanical models for these molecules are now available. For hydrogen chloride and hydrogen sulphide, however, the models are not so good but one can be content with less accurate models for these molecules since the effects studied are, in these cases, of a smaller order of magnitude. The relative positions of the molecules were found from crystal data when such were known—otherwise, the dimensions of the molecules and atoms were employed for this purpose.

In parts B, C and D, the calculation of the polarization of H_2O is described. Part B summarizes what is known from experiments about the structure of the H bond, part C gives the computation of the polarization of H_2O in the field of an adjacent H atom while part D contains the calculations of the polarization of a H-bonding H atom in the field from an adjacent H_2O molecule. Only this latter type of polarization has been calculated for the other molecules. The calculations for HF are reported in part E, for H_2S in part F and for HCl in part G. Finally, in the appendix, the calculation of certain integrals is described.

B. Structure of the H bond in water

For the study of the interaction between two water molecules, the following system has been considered:  $\diagup O'\text{—}H' \cdots O\genfrac{}{}{0pt}{}{\diagup H}{\diagdown H}$. The mutual situation of the two molecules

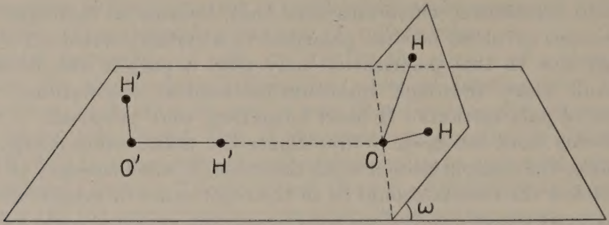


Fig. 1. Mutual situation of two water molecules in the ice structure.

is given by the ice structure proposed by Bernal and Fowler [10]. This structure was also used by Bauer and Magat [2] in their study of the electrostatic forces (cf. Fig. 1).

Each water molecule is tetrahedrally surrounded by four others. The two bonds in each molecule point towards the O-atoms of two of the surrounding molecules. This O–H ... O bond is called a hydrogen bridge or hydrogen bond. The length of the total H bond is 2.76 Å. The O–H distance in molecules situated in crystals is 0.99 Å. Hence the distance H ... O should be 1.77 Å or 3.34 atomic units (a.u.). The angle ω (54°44′) between the molecule planes (fig. 1) is given by the tetrahedral structure. Each molecule can be described by the molecular orbitals (MOs) given by Ellison and Shull [11]. These MOs seem to give a good description of the molecules. The orbital energies as well as the dipole moment agree very well with the observed values.

The present investigation includes a study of:

(i) the strengthening of the H bond which is caused by the electronic polarization of the whole H_2O molecule due to the field from the net positive charge on H′ (fig. 2);

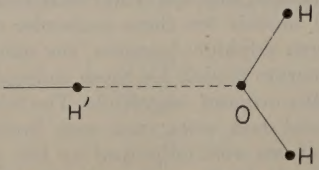


Fig. 2. That part of the system, in which polarization is considered.

(ii) the strengthening of the H bond which is caused by the polarization of H′ due to the field from the adjacent H_2O molecule (fig. 2).

C. Perturbation of the H_2O molecule

Ellison and Shull [11] have determined the best MOs, which can be found by linear combination of atomic orbitals (LCAO), for the ten electrons in the ground state of H_2O. They used the self-consistent field (SCF) method as described by Roothaan [12].

The AOs used by Ellison and Shull were Slater AOs—for the oxygen atom, 1*s*, 2*s*, 2*pz*, 2*px*, 2*py*, and, for the hydrogen atom, 1*s*. The position of the molecule in the

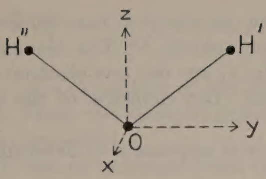


Fig. 3. Position of the H_2O molecule in the coordinate system. The molecule is assumed to be in the yz-plane.

coordinate system is shown in fig. 3. The orbital exponents were those proposed by Slater. The $2s$ orbital was made orthogonal to the oxygen $1s$ orbital.

Before the calculation of the LCAO MOs, the AOs were transformed to symmetry orbitals (SOs). These SOs belong to the same symmetry group as the molecule—in this case, the group C_{2v}. The transformation from AOs to SOs is shown in Table 2.

Table 2. Transformation of atomic orbitals into symmetry orbitals.

SO notation	AO combination	Symmetry type
σ_1	$2^{-\frac{1}{2}}(h'+h'')$	a_1
σ_2	o	
σ_3	s	
σ_4	z	
σ_5	$2^{-\frac{1}{2}}(h'-h'')$	b_2
σ_6	y	
σ_7	x	b_1

where the notations for the AOs are:

Oxygen AOs	Hydrogen AOs	
$1s$—o	$1s$—h' and h'' for the respective atoms	(2)
$2s$—s		
$2px$, $2py$, $2pz$—x, y, z		

The MOs were formed in the following way:

$$\left.\begin{aligned} \varphi(n a_1) &= \sum_{i=1}^{4} c_{ni}\,\sigma_i, \quad n=1,\dots 4,\\ \varphi(n b_2) &= \sum_{i=5}^{6} c_{ni}\,\sigma_i \quad n=5,6\\ \varphi(7 b_1) &= c_{77}\,\sigma_7. \end{aligned}\right\} \tag{3}$$

To determine the coefficients in the MOs, it is neccessary to solve the Fock equations

$$F\,c_i = \varepsilon_i\,S\,c_i. \tag{4}$$

The matrix F is the sum of the one-electron bare nuclear field energy matrix H and the total electronic interaction matrix G. The elements of the matrix S are the overlap integrals $S_{ij} = \int \sigma_i \sigma_j \, d\tau$. ε_i are the one-electron energies. In the G-part of F, the coefficients c_{pi} are involved. The elements of the column vectors c_i are the c_{ip} which are defined in (3).

To solve the equations (4), it is necessary to determine the roots ε_i of the secular equation

$$|F - \varepsilon S| = 0. \tag{5}$$

This is, in the present case, a seven-by-seven determinant. However, because of the symmetry properties of the SOs, this determinant can be simplified and the problem thus reduces to the solving of one four-by-four, one two-by-two and one one-by-one determinant. The five lowest roots ε_i of (5) are then picked out. From the corresponding c_{pi}, new matrix elements G_{ij} are computed. The process is repeated until self-consistency is attained (self-consistent field method).

The five MOs obtained with the lowest energies were: $\varphi(1a_1)$, $\varphi(2a_1)$, $\varphi(3a_1)$, $\varphi(5b_2)$, $\varphi(7b_1)$. All these MOs are doubly occupied and represent the ground state of the H_2O molecule. The final values of the c_{pi} found in this way by Ellison and Shull are listed in the second column of Table 4, see p. 264. These MOs have been obtained by finding a minimum value for the total electronic energy of the molecule. This description is then the best possible one of the type indicated in (3).

Now, we place such a molecule in a position like that shown in fig. 1. It is of course influenced in some way by its neighbour $H_2'O'$. It is assumed that the main part of this influence comes from the net positive charge of the nearest H′ atom. Such a free molecule would then have a definite potential energy in the coulomb field from this H′ atom. The total electronic energy would then be the sum of the above-mentioned electronic energy plus the energy of the electrons in this new field. However, because of the H′ net charge, the total energy of the molecule will be decreased due to a rearrangement of its electron distribution. This may be thought of as a sort of polarization of the electron cloud of the H_2O molecule. The polarization energy involved will now be calculated.

The new, perturbed MOs have been calculated in a manner similar to that in which the MOs for the free molecule were calculated. To the original H matrix, we have to add a perturbation matrix H' whose elements H'_{ij} are (cf. (8)):

$$H'_{ij} = \int \sigma_i H' \sigma_j \, d\tau. \tag{6}$$

The exchange energies between the electrons on the H′ atom and the electrons on the perturbed molecule have not been taken into consideration. A consequence of this is that the perturbing field does not enter directly into the elements G_{ij}. These elements can therefore be computed from the electron distribution of the H_2O molecule in the same way as before. The net positive charge on the H′ atom comes from the positive unit charge of its nucleus and a negative charge from the electron cloud surrounding the nucleus. As an approximation to this electron distribution, the author used a spherically symmetrical $1s1s$ distribution. The total charge of this distribution can be obtained from the population number of the H′ atom. Using Mulliken's [13] notations, this total gross atomic population on the atom H′ can be written:

$$N(\mathrm{H}') = 2 \sum_{p,i} c_{ph'} S_{h'i} c_{pi}, \tag{7}$$

where c_{pi} are the coefficients of the expansion of the MOs in the AOs of (2) and not in the SOs as in formulae (3). From the electron distribution calculated by Ellison and Shull, $N(\mathrm{H}')$ was found to be 0.8241.

An element of the matrix H' can be obtained from the following formula:

$$H'_{ij} = -(\sigma_i\sigma_j:\mathrm{N}) + 0.8241(\sigma_i\sigma_j:h'h'), \tag{8}$$

where $(\sigma_i\sigma_j:\mathrm{N})$ denotes the coulomb interaction integral for the electron distribution $\sigma_i\sigma_j$ and the H′ nucleus, and $(\sigma_i\sigma_j:h'h')$ the two-electron coulomb interaction integral for the two distributions $\sigma_i\sigma_j$ and $h'h'$. The calculation of the coulomb interaction integrals is described in more detail in the appendix. The values obtained for the elements H'_{ij} are collected in Table 3.

Table 3. Elements of the matrix H' according to (8). In a.u. (1 a.u. = 27.204 e.v.).

ij	H'_{ij}	ij	H'_{ij}
11	−0.0573	33	−0.0555
12	−0.0046	34	0.0077
13	−0.0352	37	−0.0108
14	−0.0134	44	−0.0554
17	−0.0021	47	0.0034
22	−0.0540	55	−0.0258
23	0.0000	56	−0.0192
24	0.0006	66	−0.0529
27	−0.0008	77	−0.0578

Using the new energy matrix $H^1 = H + H'$, the author performed a calculation according to the SCF-method. The symmetry of the free H_2O molecule is destroyed so that we get a mixing of the symmetry orbitals of the symmetry types a_1 and b_1. This arises from the fact that the plane of the molecule is no longer a symmetry plane. The normal plane along the molecular axis is, however, still a symmetry plane and therefore the SOs of the b_2 type are not mixed with the others in the MOs. Thus the determinant (5) now reduces to one five-by-five and one two-by-two determinant.

Since we wish to identify the new orbitals with the old ones, the same notation will be used for both of them. The occupied orbitals can then be written in the form

$$\begin{aligned}
\varphi_1 &= c_{11}\sigma_1 + c_{12}\sigma_2 + c_{13}\sigma_3 + c_{14}\sigma_4 + c_{17}\sigma_7 \\
\varphi_2 &= c_{21}\sigma_1 + c_{22}\sigma_2 + c_{23}\sigma_3 + c_{24}\sigma_4 + c_{27}\sigma_7 \\
\varphi_3 &= c_{31}\sigma_1 + c_{32}\sigma_2 + c_{33}\sigma_3 + c_{34}\sigma_4 + c_{37}\sigma_7 \\
\varphi_7 &= c_{71}\sigma_1 + c_{72}\sigma_2 + c_{73}\sigma_3 + c_{74}\sigma_4 + c_{77}\sigma_7 \\
\varphi_5 &= c_{55}\sigma_5 + c_{56}\sigma_6
\end{aligned} \tag{9}$$

Ellison and Shull [11] have found the total electronic energy of the free molecule to be 85.003_7 a.u. Since the order of magnitude of the effect studied here is about 0.0005 a.u., the energy given in [11] is not sufficiently accurate. In addition, we

Table 4. MO coefficients for the free molecule and for the molecule in perturbing fields.

	Free mol.		Perturbed mol.	
	Ellison–Shull	Present treatm.	Unsymm. perturb.	Symm. perturb.
c_{11}	−0.0033	−0.0042	−0.0042	−0.0042
c_{12}	1.0002	1.0003	1.0003	1.0003
c_{13}	0.0163	0.0169	0.0169	0.0170
c_{14}	0.0024	0.0026	0.0026	0.0026
c_{17}			0.0000	
c_{21}	0.1781	0.1781	0.1753	0.1727
c_{22}	−0.0286	−0.0286	−0.0284	−0.0282
c_{23}	0.8450	0.8450	0.8486	0.8521
c_{24}	0.1328	0.1328	0.1270	0.1212
c_{27}			0.0102	
c_{31}	0.3341	0.3340	0.3325	0.3330
c_{32}	−0.0258	−0.0258	−0.0258	−0.0258
c_{33}	−0.4601	−0.4600	−0.4494	−0.4449
c_{34}	0.8277	0.8278	0.8241	0.8317
c_{37}			−0.1125	
c_{71}			0.0256	
c_{72}			−0.0018	
c_{73}			−0.0514	
c_{74}			0.0981	
c_{77}	1	1	0.9936	1
c_{55}	0.7759	0.7759	0.7698	0.7636
c_{56}	0.5428	0.5428	0.5478	0.5529

cannot be certain that the MOs (3) published by Ellison and Shull are sufficiently self-consistent for our purpose because we have to use integrals given in their tables with an accuracy of only four decimal places. Since the present calculation is based on the assumption that the free molecule has an absolutely minimized energy, it is necessary to perform some further SCF-cycles for the free molecule to ensure that the MOs we start with, together with the integrals used, are satisfactorily consistent. The final coefficients found here are listed in the third column of Table 4. It is seen that they do not differ much from those given by Ellison and Shull which are listed in the second column of Table 4. Finally, the set of coefficients obtained for the perturbed molecule are listed in the fourth column of Table 4. The total energy of the free molecule was found to be 85.0031_7 a.u. The one-electron energies obtained here are given in Table 5 together with those of Ellison and Shull.

The potential energy of the unperturbed molecule in the field from the net positive charge on H′ was calculated to be -0.53892 a.u. Adding this energy to the free molecule electronic energy, we get a total electronic energy of -85.54209 a.u.

This energy must be compared with that obtained from the calculation of the best possible MOs (9) in the perturbing field. This latter energy is -85.54238 a.u. The

Table 5. One-electron energies obtained in the present treatment compared with those given by Ellison–Shull. In a.u.

	One-electron energies	
	Ellison–Shull	Present investigation
1	−20.485	−20.4851
2	− 1.330	− 1.3302
3	− 0.485	− 0.4852
5	− 0.682	− 0.6817
7	− 0.433	− 0.4335

energy gain from the polarization is the difference between these two energies, viz. 0.00029 a.u. or 0.18 kcal/mole.[1]

Another, perhaps even more, interesting problem is that of one water molecule perturbed by two other molecules, due to H atoms situated symmetrically with respect to the molecular plane. In the ice crystal, the "central" molecule has, as well as the adjacent molecule $H_2'O'$, another neighbour $H_2''O''$ in a position similar to that of $H_2'O'$ but on the opposite side of the H_2O-plane (cf. fig. 4). The problem is now to determine to what extent the two atoms H′ and H″ are able to polarize the H_2O molecule.

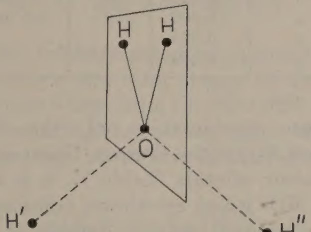


Fig. 4. Position of the atoms in the symmetrical case. H′OH″ in the plane of the paper. HOH perpendicular to the plane of the paper.

In this case, the system has the same symmetry as the free molecule. Therefore, the MOs are linear combinations of the same SOs as in the free molecule. Except for the H matrix, everything is identical with the free molecule case.

The new matrix H^1 is the sum of the matrix H for the free molecule and the perturbation H'. The elements H'_{ij} appear in Table 6. They are twice the corresponding elements in the unsymmetrical case (Table 3) with the exception of those where $\sigma_i\sigma_j$ is a distribution with b_1 symmetry, in which case they are zero.

An SCF calculation similar to that described above gives the values for the coefficients which are shown in the fifth column of Table 4. The energy of the unpolarized molecule in the field is −86.08104 a.u. The energy resulting from the SCF calculation was found to be −86.08138 a.u. The gain in energy due to polarization is therefore 0.00034 a.u. or 0.21 kcal/mole.

We have, however, reason to believe that the polarization in question is considerably larger than what has been computed using the method described. In this

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[1] One atomic unit of energy equals 627 kcal/mole.

Table 6. Elements of the perturbation matrix in the symmetrical case. In a.u.

ij	H'_{ij}	ij	H'_{ij}
11	−0.1147	33	−0.1109
12	−0.0092	34	0.0153
13	−0.0705	44	−0.1107
14	−0.0268	55	−0.0517
22	−0.1079	56	−0.0384
23	0.0001	66	−0.1058
24	0.0012	77	−0.1156

Table 7. The MOs of Ellison-Shull transformed to equivalent orbitals (EOs). $\varphi\ (b\pm)$ are the two bonding orbitals and $\varphi\ (l\pm)$ the two lone-pair orbitals.

EO $\varphi\ (b\pm)$		EO $\varphi\ (l\pm)$	
AO	Coeff.	AO	Coeff.
h'	0.577	o	−0.009
h''	−0.199	s	0.680
o	−0.026	z	−0.192
s	−0.006	x	±0.707
z	0.561		
y	±0.384		

method, we have taken into consideration only the change in the original MOs without including the excited AOs of the O atom. Upon expressing the electron distribution by means of equivalent orbitals (Table 7), it is seen that the free H_2O has already two filled lone-pair MOs which are almost completely localized at the "back" of the O atom. Thus, the computed electron density at the "back" of the O atom cannot increase as a result of the perturbing potential unless excited AOs are included in the changed MOs. However, for computational reasons we assume the changed MOs to be linear combinations of the same AOs as were used in the original MOs. Consequently, our calculation can only take into account that part of the effect from the adjacent H atoms which results in a movement of the electrons of the O–H bond closer towards the O atom. Hence, these considerations indicate that this perturbing effect would give a much larger energy gain if the excited AOs of the O atom were included.

D. Polarization of H′ in the field from H_2O

The second effect studied here is the polarization of the H′ molecule in the field from the adjacent H_2O. This investigation is performed under the assumption that the electron cloud around the H′ atom is polarized in the same way as it would be if the atom was free. This simplification may be justified since we only want results of the correct order of magnitude. The result obtained using this free atom approximation may afterwards be modified by a factor which accounts for the fact that the electron charge around the H′ atom in the molecule is a little smaller than one.

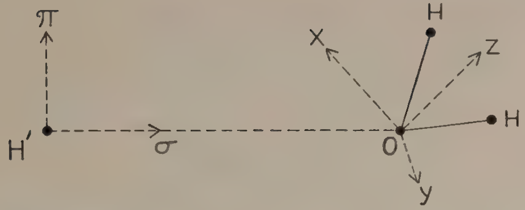

Fig. 5 (cf. fig. 1). Mutual positions of H' and the perturbing molecule H_2O. σ, π, x and z-directions in the plane of the paper.

The $1s$ atomic orbital of the original H' is replaced by a hybrid of the three AOs, $1s$, $2p\sigma$ and $2p\pi$. The $2p$ AOs have orbital exponents 0.5. The σ-direction is along the H' ... O line. The π-direction is perpendicular to this line and is in the zx-plane (fig. 5). This new wave-function for the electron around H' can be written in the following way:

$$\psi = (1 + \lambda^2 + \mu^2)^{-\frac{1}{2}} (1s + \lambda\sigma + \mu\pi), \tag{10}$$

where the following abbreviated notations for the AOs around H' have been used:

$$1s \rightarrow s, \quad 2p\sigma \rightarrow \sigma, \quad 2p\pi \rightarrow \pi. \tag{11}$$

The coefficients λ and μ can be determined by means of a variation method. The energy that is to be minimized is the total energy of the electron distribution $\psi^* \psi$ obtained from (10) in the coulomb field from the H_2O molecule. No exchange energies between the electrons on H' and H_2O have been taken into account.

The energy to be considered can be written in the following form:

$$E = \frac{1}{1+\lambda^2+\mu^2} \{E_s + (\mathrm{M}:ss) + 2\,\lambda\,(\mathrm{M}:s\,\sigma) + 2\,\mu\,(\mathrm{M}:s\,\pi) + \\ + \lambda^2\,[E_p + (\mathrm{M}:\sigma\,\sigma)] + 2\,\lambda\,\mu\,(\mathrm{M}:\sigma\,\pi) + \mu^2\,[E_p + (\mathrm{M}:\pi\pi)]\}, \tag{12}$$

where (M:ab) is the total coulomb interaction energy between the H_2O molecule and the electron distribution ab. (M:ab) is composed of terms representing the interactions of the distribution ab with the nuclei and the electrons of the molecule:

$$(\mathrm{M}:a\,b) = 2\sum_{pij} c_{pi}\,c_{pj}\,(\sigma_i\,\sigma_j:a\,b) - (\mathrm{O}:a\,b) - 2\,(\mathrm{H}:a\,b), \tag{13}$$

where the sum over p is to be taken over all MOs and the sums over i and j over all SOs. $(\sigma_i\sigma_j:ab)$ is the coulomb interaction integral for the distributions $\sigma_i\sigma_j$ and ab, and (O:ab) and (H:ab) represent the corresponding interactions between the distribution ab and the nuclei O and H. The values for (M:ab) are tabulated in Table 8. The energies E_s and E_p in (12) are the orbital energies of electrons in the $1s$ and $2p$ states respectively. They have the values: $E_s = -\frac{1}{2}$, $E_p = -\frac{1}{8}$.

Most of the integrals have been evaluated using standard methods. Approximations to the three-center integrals have been obtained by different methods. The integral calculations are described in more detail in the appendix.

Table 8. (M:*ab*) according to (13) for H_2O. In a.u.

$a\,b$	$(M\!:\!a\,b)$
ss	0.0490
$s\sigma$	−0.0228
$s\pi$	−0.0093
$\sigma\sigma$	−0.0632
$\sigma\pi$	−0.0122
$\pi\pi$	0.0122

Using the values (M:*ab*) given in Table 8, the energy E in a.u. can now be expressed in the following form:

$$E = \frac{1}{1+\lambda^2+\mu^2}\,(-0.4510 - 2\,\lambda\,0.0228 - 2\,\mu\,0.0093 - \lambda^2\,0.1882 - 2\,\lambda\,\mu\,0.0122 - \mu^2 0.1128).$$

Its minimum with respect to λ and μ has been computed with neglect of terms of the third order or more in λ, μ. The roots obtained are $\lambda = 0.088$, $\mu = 0.031$ and the minimum energy is $E_{\min} = -0.4533$. The gain in energy is thus $E_0 - E_{\min} = -0.4510 - (-0.4533) = 0.0023$ (a.u.) or 1.44 kcal/mole.

Thus, the total computed energy gain due to polarization effects is 0.2 kcal/mole from effect (i) and 1.44 kcal/mole from effect (ii). As mentioned before, this latter value should be modified by a factor which accounts for the real electron charge on H′. This factor is 0.82 according to (7). The resulting energy from (ii) should therefore be 1.2 kcal/mole and the total effect from (i) and (ii) 1.4 kcal/mole.

However, this value is, as has earlier been remarked, not very definite. There are several factors which might modify it in one direction or the other. One factor, which could increase it, is the fact that energies obtained by a minimizing procedure, are always lower limits for the correct values. For example, when calculating the polarizability of an H atom in a homogeneous electrical field, the use of an electron wave function $\alpha 1s + \beta 2p$ gives a result about 30 % lower than the correct value. Therefore, assuming the electron to be excited higher than to $2p$ states, this polarization should be appreciably larger than 1.2 kcal/mole. The value 0.2 kcal/mole for the effect (i) has been discussed at the end of part C. One factor which would decrease the value, is the fact that the effect (ii) should cause a slight weakening of the O′–H′ bond.

Although the value $0.2 + 1.2 = 1.4$ (kcal/mole) for the total polarization energy is rather approximate, it is interesting to compare it with the purely electrostatic energy. Using the point charge model, discussed by Bauer and Magat [2], this energy can be calculated to be 5.1 kcal/mole. Another calculation by Pople [14] gives 5.95 kcal/mole for the electrostatic energy between two water molecules. Thus, it is seen that the polarization energy is not a negligible part of the total H bond energy when water is one of the constituents.

E. Hydrogen fluoride

For the molecules HF, H_2S and HCl, only the effect (ii) has been investigated.

Hydrogen fluoride contains very strong H bonds. Its melting point is −92°C and the heat of polymerization 6.7 kcal/mole. The molecules form long zig-zag chains which are present in both the crystal and vapour states [15].

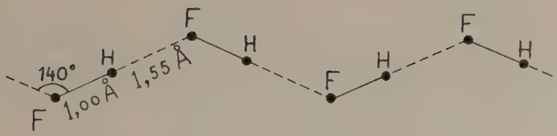

Fig. 6. The zig-zag structure of HF. This model with HFH angle of 140° and F–F distance of 2.55 Å is used in the present investigation.

In the vapour, the H–F–H angle is about 140° and the H bond length, i.e. the distance F–F, is about 2.55 Å. These values are taken from J. H. Simons, *Fluorine Chemistry* [15], where it is also remarked that the H atoms are in line with the fluorine atoms at least within ± 15°.

The model used in the present study is that shown in fig. 6 with F–H–F on a straight line, the angle H–F–H being 140° and the distance F–F 2.55 Å. The distance F–H in the chain has been found to be 1.00 ± 0.06 Å and therefore 1.55 Å is used for the H ... F distance in this investigation.

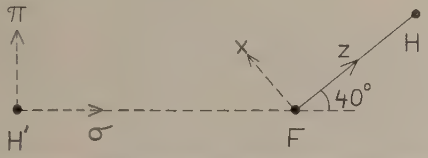

Fig. 7. Mutual positions of H′ and the perturbing molecule HF. All directions in the plane of the paper. Cf. fig. 5.

Here the polarization of the H′ atom in the field from the HF molecule (see fig. 7) is to be calculated (cf. the calculation on water in part D). For the description of the molecule, the MOs calculated by Allen and Karo [16] have been used. Their best MOs are LCAO MOs found by a single determinant self-consistent field procedure. The AOs in these MOs are the hydrogen 1*s*, denoted *h*, the fluorine 1*s*, 2*s*, 2*px*, 2*py* and 2*pz*, denoted *o*, *s*, *x*, *y* and *z* respectively, with *s* and *o* orthogonal to each other.

The LCAO MOs, given by Allen and Karo, are:

$$\begin{aligned}
\varphi_1 &= 0.004615\,h - 1.000147\,o - 0.015878\,s - 0.002451\,z \\
\varphi_2 &= 0.164605\,h - 0.022087\,o + 0.902826\,s + 0.091382\,z \\
\varphi_3 &= -0.576625\,h + 0.028136\,o + 0.461584\,s - 0.685841\,z \\
\varphi_4 &= x \\
\varphi_5 &= y
\end{aligned} \tag{14}$$

The orbital energies are:

$$\begin{aligned}
\varepsilon_1 &= -26.14352 \quad \text{a.u.} \\
\varepsilon_2 &= -1.480349 \quad ,, \\
\varepsilon_3 &= -0.568109 \quad ,, \\
\varepsilon_4 &= -0.466318 \quad ,, \\
\varepsilon_5 &= -0.466318 \quad ,,
\end{aligned}$$

We now assume that the electron wave function ψ for H′ has the form (10) as in the water case. Here s, σ and π are, as before, abbreviated notations for the H′ functions 1s, 2$p\sigma$ and 2$p\pi$. The calculations are performed in the same way as in the water case. The total energy which is to be minimized is given by (12). In the present case, (M:ab) can be written:

$$(\mathrm{M}:a\,b) = 2\sum_{pij} c_{pi}\,c_{pj}\,(\sigma_i\,\sigma_j : a\,b) - (\mathrm{F}:a\,b) - \mathrm{H}:a\,b) \tag{15}$$

in analogy to (13). The calculation of the integrals is described in the appendix and the (M:ab) finally obtained are given in Table 9.

Table 9. (M:ab) for HF in a.u.

$a\,b$	(M:$a\,b$)
$s\,s$	−0.0073
$s\,\sigma$	−0.0337
$s\,\pi$	−0.0003
$\sigma\,\sigma$	−0.0774
$\sigma\,\pi$	−0.0057
$\pi\,\pi$	0.0020

On minimizing the energy, we find that the parameter values at the minimum are $\lambda = 0.107$, $\mu = 0.002$, corresponding to the value $E_{\min} = -0.5109$. For $\lambda = 0$, $\mu = 0$, the energy is -0.5073. The energy gain due to polarization is therefore 0.0036 a.u. or 2.28 kcal/mole.

In order to take into consideration the fact that the H′ nucleus in H′F′ does not have a complete electron around it, one should multiply the polarization energy obtained above by the gross atomic population of the H′ atom according to (7). From the coefficients of (14) and the values of the overlap integrals, we find the factor 0.85. The corrected value for the electronic polarization energy is thus $0.85 \times 2.28 = 1.9$ (kcal/mole).

For HF as well as H_2O, we have calculated a considerable polarization of the H′ atom. The calculations for H_2O indicate a somewhat smaller effect from the polarization of the whole molecule. In the HF case, we have not tried to estimate the latter effect. However, the MOs and the orbital energies are very similar to the corresponding quantities for H_2O and the perturbing fields from H′ are rather similar to each other. We have therefore good reasons to believe that the effects in question are of the same orders of magnitude in the two cases.

F. Hydrogen sulphide

The polarization of the H′ electron has also been estimated for H_2S and HCl. Although these molecules usually do not contain H bonds, we will assume a situation which would be most favourable for H bonding.

H_2S solidifies at −82.9°C and is assumed to be arranged in a cubic closest packing structure (ref. 1, page 375). From this structure, the mean distance 4.37 Å between the molecules can be calculated. The assumed H bond has the configuration indicated

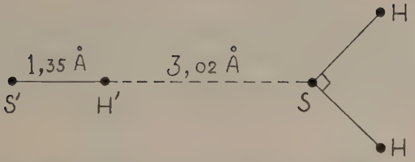

Fig. 8. Assumed mutual positions of two H_2S molecules. All the atoms are in the plane of the paper.

in fig. 8. The bond length 1.35 Å for S–H and the van der Waals radii of H and S, 1.20 and 1.85 Å respectively, are given by Pauling [1]. By summing these distances we get a total S–S distance of 4.40 Å. This agrees well with the value 4.37 Å obtained from density measurements on solid sulphur. The value 4.37 Å is used in the following calculations. For simplicity, the perturbing molecule H_2S is allowed to lie in the same plane as the perturbed H′. The bond angle is 92°20′ (ref. 1, p. 79) but in these computations we use the value 90°.

The electron distribution of a free H_2S molecule can be described by means of Slater AOs from which a rather rough model can be set up. We assume the S orbitals $1s$, $2s$, $2p$, $3s$ and $3pz$ to be filled (fig. 9). The remaining four electrons are supposed to occupy the two bond orbitals φ_1 and φ_2, where $\varphi_1 = \alpha 3px + \beta h_x$, $\varphi_2 = \alpha 3py + \beta h_y$. h_x and h_y are $1s$ wave functions centered at H_x and H_y respectively (fig. 9).

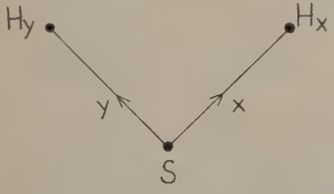

Fig. 9. The perturbing H_2S molecule.

The reason why we have not let the bond orbitals involve $3s$ is as follows. For the water molecule, which is the most similar one to H_2S, the MOs when transformed to equivalent orbitals (Table 7) have hardly no $2s$–h mixing. This means that the overlap population $2sh$ is practically zero. Therefore the above-mentioned choice of bond orbitals may be as good as those involving $3s$.

The two parameters α and β are chosen so that the total molecular dipole moment is correct. (0.93 D.) The sign of it, however, cannot be determined experimentally but, from the electronegativity scale, it is reasonable to assume that the H atoms should be more positive than the S atom. The bond dipole arrow should then point in the S–H direction.

The electron configuration can now be written:

$$\left.\begin{array}{c} 1s^2\, 2s^2\, 2p^6\, 3s^2\, z^2\, \varphi_1^2\, \varphi_2^2, \\ \text{where} \quad \varphi_1 = 0.7161\, x + 0.4315\, h_x, \qquad \varphi_2 = 0.7161\, y + 0.4315\, h_y \end{array}\right\} \tag{16}$$

The following abbreviated notations have been used: z for $3pz$, x for $3px$, y for $3py$.

In the same way as for water and hydrogen fluoride, the polarization of the electron cloud around H′ due to partial excitation to $2p$ is calculated. The electron wave function around H′ is supposed to assume the form

$$\psi = (1+\lambda^2)^{-\frac{1}{2}}\,(1s+\lambda\, 2p\sigma), \tag{17}$$

where σ is in the H′ ... S direction. Because of the symmetry, the $2p\pi$ cannot enter into ψ.

The total energy of the electron described by ψ is minimized. This energy is given by the following formula in analogy to (12):

$$E = \frac{1}{1+\lambda^2}\{E_s + (\mathrm{M}:s\,s) + 2\,\lambda\,(\mathrm{M}:s\,\sigma) + \lambda^2\,[E_p + (\mathrm{M}:\sigma\,\sigma)]\}. \tag{18}$$

The (M:ab)s can in this case be written (cf. (13) and (15)):

$$(\mathrm{M}:a\,b) = 2\sum_{pij} c_{pi}\,c_{pj}\,(\sigma_i\,\sigma_j:a\,b) - (\mathrm{S}:a\,b) - 2\,(\mathrm{H}:a\,b) \tag{19}$$

and the numerical values are given in Table 10.

Table 10. (M:ab) for H_2S. In a.u.

ab	(M:$a\,b$)
$s\,s$	0.0224
$s\,\sigma$	−0.0051
$\sigma\,\sigma$	−0.0361

The energy minimum is −0.47765 a.u. for $\lambda = 0.016$. The energy for $\lambda = 0$ is −0.47757 a.u. Therefore the energy gain is 0.00008 a.u. or 0.051 kcal/mole. This result, however, depends to a great extent upon the value of one of the approximated three-center integrals. The value of the coulomb interaction integral (xh_x:$s\sigma$) is, with a point charge approximation, 0.0062 a.u. Using this value, the above-mentioned energies are obtained. The Mulliken approximation of the integral gives 0.0084 a.u. This approximation, however, can almost certainly be expected to give too high a value. It admittedly replaces the proper xh_x distribution with another of the same total charge but, on the other hand, it supposes a positive value for the electron "density" at every point. Roughly speaking, it means that one changes the xh_x distribution by moving electrons from one side of the S atom to the other. When the Mulliken approximation value of the integral is inserted into the total energy, one finds a very small polarization energy of about 0.0003 kcal/mole.

Even if we use a value for the integral mentioned which is incorrect by 10 or 20 %, the polarization can still not be much larger than 0.05 kcal/mole.

G. Hydrogen chloride

The melting point of HCl is −112°C. Its structure is cubic closest packing except at very low temperatures where the structure is modified so that the molecules do not rotate freely. Hornig and Osberg [17] have found by studying the infrared spectrum at −205° that it forms zig-zag chains similar to those found in gaseous and crystalline HF. This indicates that the structure is to some extent based on hydrogen bonds at very low temperatures. The melting and boiling points are much lower than for HF and this is in agreement with the assumption of weak H bonds.

The author has studied two HCl molecules which are situated along the same straight line (fig. 10). Since the effect is very small, this simplified model gives sufficiently reliable values.

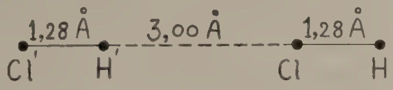

Fig. 10. Assumed mutual positions of the two adjacent HCl molecules.

Since the structure is rather indefinite, the bond distances were chosen according to the data on H–Cl bond and van der Waals radii tabulated by Pauling [1]. The van der Waals radii of H and Cl are 1.20 and 1.80 Å respectively. This gives a total H ... Cl distance of 3.00 Å. The inner electrons of the Cl atom are supposed to occupy the usual Slater AOs in the first two shells. The $3px$ and $3py$ are doubly occupied while the four remaining electrons are supposed to form one lone-pair MO, $3l$, and one bond orbital, $3b$ (fig. 11).

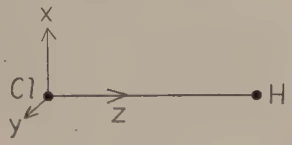

Fig. 11. The directions x, y, z in relation to the HCl molecule.

The Cl part of $3b$ is taken as the s,p-hybrid orthogonal to $3l$ and thus we can write the orbitals in the following way:

$$3\,l = \tfrac{1}{2}\,(s - z), \qquad 3\,b = \alpha\,(s + z) + \beta\,h. \tag{20}$$

s stands for $3s$, z for $3pz$ and h for hydrogen $1s$. The parameters $\alpha = 0.2374$ and $\beta = 0.7430$ were chosen so that they give the correct dipole moment. Its value is 1.1 debye, but the sign of it cannot be determined experimentally. The possibility that its direction is from H to Cl can, however, be excluded on semiempirical grounds [18].

The configuration for HCl is then: $1s^2 2s^2 2p^6 3px^2 3py^2 3l^2 3b^2$. The electron cloud around H′ is now described by a wave function ψ of the same form as that in the H_2S case (17). Its total coulomb interaction energy has also the same form as that in the H_2S case and is given by (18), where:

$$(\mathrm{M}:a\,b) = 2\sum_{pij} c_{pi}\,c_{pj}\,(\sigma_i\,\sigma_j : a\,b) - (\mathrm{Cl}:a\,b) - (\mathrm{H}:a\,b) \tag{21}$$

in analogy to (13), (15) and (19). (M:ab) is tabulated in Table 11.

Table 11. (M:ab)s of HCl. In a.u.

ab	(M:ab)
ss	0.0187
$s\sigma$	−0.00029
$\sigma\sigma$	−0.0605

Upon minimizing the energy, it is seen that it can only be decreased by a negligible amount due to polarization. Using the computed values of the integrals, it can be found that the energy gain would be 0.0002 kcal/mole. However, this figure is comparatively unreliable. For small changes in some integrals, it could increase by quite a large factor. The uncertain integrals which could most affect the energy gain are the three-center integrals (sh:$s\sigma$) and (zh:$s\sigma$). The error in these integrals may be ± 25 %. The greatest deviation, when both integrals are either too large or too small by 25 %, gives an energy gain amounting to about 0.02 kcal/mole. Therefore, with this model, we can hardly obtain an energy gain due to polarization which could play an important part in the formation of H bonds. Unfortunately we do not have so good models as were available for water and hydrogen fluoride, but it does not seem possible that we would get an appreciably greater energy than 0.02 kcal/mole with any other reasonable model.

H. Conclusions

In Table 12, the parameters λ and μ are collected together with the corresponding polarization energies. It is interesting to notice the direction of the electron displacements around the H′ atom. This direction is given by the two parameters λ and μ and is shown in fig. 12 for H_2O and HF.

Table 12. Polarization parameters λ, μ and energies from polarization of H′.

	H_2O	HF	H_2S	HCl
λ	0.088	0.107	~0.02	~0.01
μ	0.031	0.002	—	—
$\sqrt{\lambda^2+\mu^2}$	0.093	0.107	~0.02	~0.01
Energy decrease. In kcal/mol.	1.2	1.9	0.05	0.01

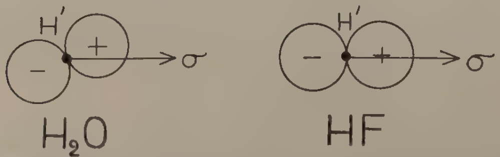

Fig. 12. Displacement of the H′ electron cloud for H_2O and HF with complete models for the perturbing molecules.

In both cases, the electrons are displaced towards the perturbing molecule. From the directions of the dipole moments of these molecules, one should expect the electrons around H′ to be repelled by the molecule. However, the positive charges of the molecule are point charges while the negative charges are spread out over a large volume and this causes the attraction from the positive charges to dominate over the repulsion from the negative charges.

The net result is, therefore, that the electron around H′ is displaced towards the molecule. The direction shows a deviation from the H′ ... O and H′ ... F lines respectively and this effect can to some extent be due to the dipole moment direction.

When the distance between the molecules is increased, we can expect the dipole character of the perturbing molecule to exert a greater influence. Hence, at very large distances, a change in sign of the parameter λ should occur. The very weak effect in the HCl case can be explained in this way. λ is very nearly zero and in fact we do not know with certainty which sign it has. If the HCl molecules were further apart, then λ would be negative and the effect would increase somewhat before decreasing to zero at an infinite distance.

This shows that a calculation of the polarization effect by approximating the molecules to point charges is inadequate.

This is shown concretely in a calculation of the polarization of H′, which has been performed in the H_2O case with a very rough point charge model for H_2O. The molecule was approximated by means of a charge $-2q$ at the O nucleus and two charges q at the two H nuclei. q was given a value which gave the correct dipole moment. In this case, the electron cloud around H′ was displaced in a direction given by $\lambda = -0.03$, $\mu = 0.01$ (fig. 13). The energy gain from the polarization was much smaller than in the calculation with the complete electron distribution, viz. only 0.29 kcal/mole.

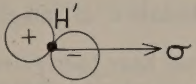

Fig. 13. Direction of displacement with point charge model for H_2O.

One should therefore be very cautious when approximating continuous electron distributions by means of point charges, especially when the interacting systems lie close together and the deviation of the electron clouds from the point charge approximation is relatively large. However, with additional point charges placed at other points, e.g. the centers of gravity of lone-pair electrons, bonding electrons etc., one should get rather reliable results.

Finally, the contribution of electrostatic interaction to the energy of the H bonds was investigated. The same mutual positions of the molecules as before were considered. Quite aware of the risk of using point charge models, we approximated the molecules by point charges at the nuclei of the molecule in question. This approximation can be expected to account better for the electrostatic energies between whole molecules than for the forces upon electron distributions, situated near-by, like those in the examples discussed just above. The magnitudes of the point charges were determined so that they gave the proper dipole moments. For water we have, as a comparison, the value 5.95 kcal/mole computed by Pople [14] with a somewhat more reliable point charge model. These electrostatic energy values appear in Table 13 where they can be compared with the polarization energies.

Table 13. Contribution of polarization and electrostatic energies to H bond energy. In kcal/mole.

	H_2O	HF	H_2S	HCl
El.stat. energy	5.1	7.5	0.25	0.50
Polarization of molecule, eff. (i) . .	0.2			
Polarization of H′ eff. (ii)	1.2	1.9	~0.05	~0.01
Exp. H bond energy	5.8	6.7	—	—

For the H bond-forming compounds H_2O and HF, we have found, as is seen in Table 13, contributions to hydrogen bond energies from polarization which are of the same orders of magnitude as experimental H bond energies. For H_2O, HF and H_2S, the polarization energies are also of the same orders of magnitude as the probable electrostatic energies. For the latter substance, however, the energies are not sufficient to cause stable H bonds since such bonds require energies of at least a few kcal/mole.

ACKNOWLEDGEMENTS

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APPENDIX

Calculation of integrals

One-electron two-center integrals have been calculated by conventional methods, most of them with the aid of Rosen's A- and B-functions.

$2s$ and $2p$ two-electron two-center coulomb integrals have been computed by means of Roothaan's tables [19]. For parameter values which are not included in these tables, the integrals have been expanded into A- and B-functions. For H_2S and HCl where we have supposed the second shell to be filled, we only need integrals of the type $(2s2s{:}ab)$. In these two cases, the $2s$ orbital exponents are large and therefore some of the integrals have been calculated using a point charge approximation for the $2s2s$ distribution. The Cl and S $1s1s$ distributions are included in the nuclei.

Of the integrals involving electrons in the third shell, some have been calculated exactly with the aid of A- and B-functions, viz. those of the types $(3s3s{:}ab)$ and $(\sigma_i\sigma_j{:}ss)$ where σ_i and σ_j denote S and Cl $3s$ and $3p$ wave functions and ab H′ wave functions. For the computation of the remaining third shell integrals, we approximate the distributions $3s3pz$, $3px3px$, $3py3py$ and $3pzpz$ by means of two point charges one on each side of the nucleus. The values obtained from these two point charges are then modified with a factor which accounts for the diffuseness of the actual distribution.

The two-electron three-center integrals have been approximated in different ways. In the water case, great use has been made of the discussions on different three-center integrals given by Ellison [20].

H_2O and HF.

The water electron distribution oh' has been approximated by means of a point charge with the proper magnitude and electric moment. For water, these integrals are also compared with the so-called Löwdin approximation,[1] which gave exactly the same results. Because of this, the Löwdin approximation was used for the corresponding HF integrals.

The distribution sh' has been approximated in the same manner and a comparison indicates a good agreement between the Löwdin approximation and a modified point charge approximation. This modification implies that the energy obtained with the pure point charge is multiplied by a factor

$$k=\frac{1}{2}\left\{\frac{(ss:ab)}{(\mathrm{N}:ab)}+\frac{(hh:ab)}{(\mathrm{H}:ab)}\right\} \tag{22}$$

where N denotes the nuclei F and O respectively. For the water distribution $h'h''$ integrals, the Mulliken approximation has been used. The values were also computed by means of a method used by Ellison for similar integrals; the integrals are expressed as linear functions of the angle HH'H (fig. 14).

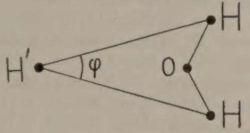

Fig. 14. The angle φ used in formula (23).

$$I=a\varphi+b. \tag{23}$$

The parameters a and b were determined by use of well-known integral values for $\varphi=0$ and π. The values obtained in this way agree rather well with those from the Mulliken approximation.

The distributions $2pzh'$ and $2pyh'$ have been approximated by Ellison [20] using homogeneous, charged spheres and such spheres have also been used by the author. Their radii were determined in such a manner that certain simpler two-electron integrals, which can be computed by other methods, get the proper values in the sphere approximation. In the same way, spheres representing electron clouds around H' were determined. The actual integrals were then approximated by means of the coulomb interaction energies between the sets of charged spheres. The corresponding integrals in the HF case have been computed with the aid of point charge approximations. The electron cloud $2pzh$ was replaced by two point charges; one, $-Q_1$, representing the negative part of the distribution in the maximum of this distribution at the "back" of F and the other, Q_2, representing the positive part in the maximum of this part between F and H. The energy obtained in this way is thereafter modified with a factor as described earlier for $(sh:ab)$ integrals (22).

---

[1] The distribution $\chi_1\chi_2$ is approximated by $\lambda_1\chi_1\chi_1+\lambda_2\chi_2\chi_2$. λ_1 and λ_2 were calculated so as to give proper total charge and charge moment.

H_2S and HCl.

The three-center integrals which appear are $(3ph:ab)$ with $3p$ directed along the bonds S–H and Cl–H respectively and, in the HCl case, $(3sh:ab)$. For the latter integral, the Mulliken and Löwdin approximations agree rather well. For the $3ph$ distribution, the Mulliken approximation cannot be expected to be good because the proper distribution has a negative part which this approximation does not take into account. The Löwdin approximation is somewhat better in this respect and is used for these integrals except for those involving the H′ distribution $s\sigma$. The exactness of these integrals is more important because they enter into the total energy expression in the term containing λ to the first order. These integrals are therefore also computed with point charge approximations.

Most of the A- and B-integrals have been computed using Flodmark's tables [21]. Linear interpolation in these tables was usually sufficient to give the integrals with accuracy in 4–6 figures.

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